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SOME TOPICS IN APPLIED ELECTROCHEMICAL KINETICS, (U)
JUL 80 E J CASEY, J R COLEMAN, W A ADAMS

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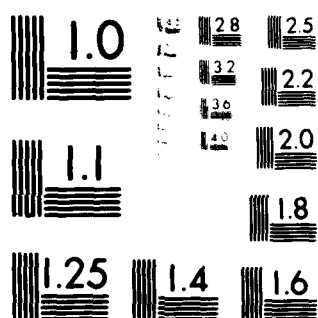
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DREO REPORT NO. 829
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SOME TOPICS IN APPLIED ELECTROCHEMICAL KINETICS

by

E.J. Casey, J.R. Coleman and W.A. Adams



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DEPARTMENT OF NATIONAL DEFENCE
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DEFENCE RESEARCH ESTABLISHMENT OTTAWA

REPORT NO. 829

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67 SOME TOPICS IN APPLIED ELECTROCHEMICAL KINETICS;

by
10 E.J./Casey/J.R./Coleman and W.A./Adams
Energy Conversion Division
Defence Research Establishment Ottawa

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JULY 1980
OTTAWA

* Invited Lecture. Prepared for the "Symposium on Chemical Kinetics", held in honor of Prof. K.J. Laidler at the Annual Conference of the Chemical Institute of Canada, Ottawa, June 1980.

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ABSTRACT

The designer of an electrochemical reactor attempts to minimize the inevitable energy losses associated with irreversible processes. The slow steps, which are the greatest offenders, have to be identified. Fortunately, diagnostic techniques have arisen from developments in electrochemical kinetics -- not only for electrode processes but also for the mass-transfer and phase-separation processes which occur in series and parallel in every electrochemical reactor.

Although electroplating, anodizing and electromachining, electro-winning and electrosynthesis are acknowledged as activities also of great importance to Canadian life, in this paper the examples will be drawn from the authors' work on batteries and fuel cells, i.e. from attempts to identify the slow steps and the wasteful side reactions, and to design around them.

The mutual influence of theoretical ideas and practical achievements is the unifying theme of this lecture.

RÉSUMÉ

Toute réaction électrochimique qui se produit à une vitesse définie souffre de pertes d'énergie. On a intérêt à réduire au minimum ces pertes dans le cas des processus électrochimiques appliqués. Des techniques de cinétique électrochimique permettent d'identifier les étapes d'une réaction qui limitent sa vitesse.

Les auteurs étudient des batteries et piles à combustible depuis plusieurs années et, dans cette communication, ils indiquent les sources de pertes d'énergie dans un système électrochimique qu'ils ont analysé. Des exemples de tentatives d'augmenter l'efficacité de quelques processus électrochimiques seront également présentés.

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INTRODUCTION

In preparing this paper we have made some assumptions in answer to the question: What topics might the Honored Guest and the likely audience like to hear discussed at this point in the Symposium?

We have assumed that the terminology of electrochemistry may not be as familiar as the listener might like. We have assumed that a general overview might be more useful and lasting than a report on a detailed narrow investigation. We have assumed that you would like to know a bit about what our laboratory has been up to in recent years. Finally we thought that you might be interested in knowing something about at least one object of our recent personal attention.

Although ours is a laboratory of applied research, we do try to look at things from a fundamental as well as a practical point of view. We do find the dual approach stimulating: they do support each other.

The general reader or audience may find it strange that an invited paper should bear the names of three authors. The reason is that Adams, Coleman and Casey were all students of Laidler at one time and that the three-body collision -- always improbable -- which occurs daily in our laboratory may be significant for that reason if for no other!

The talk consists of four parts. 1st a tutorial on terminology in which we try to bridge a communications gap between applied electrochemists and general physical chemists; 2nd a demonstration and discussion of one simple electrochemical reactor; 3rd a litany of current interests in sulfur-compounds; and 4th a few facts about an investigation of the feasibility of constructing cells based on electrolytes composed of salts which are liquid at room temperature. Figure 1 gives the outline.

CROSSTALK

The term "kinetics of electrochemical processes" is a widely used but an imprecise expression. It is an all-encompassing concept including rates and mechanisms of all the consecutive and parallel processes or steps which operate in the reactor. The term "reactor" is also a very general one

and is used here to mean any electrochemical cell in which electrochemical processes are occurring. The reactor may be for electroplating, for a transport measurement, for electropolishing; or it may be a battery of cells for storage of electrical energy; or it may be a cell for the production of chemicals such as hydrogen or chlorates or other inorganics; or it may be for the production of organics like aniline. In a sense even a corroding piece of metal in some hostile environment could be called a reactor, as could a living cell in which the electrochemical process of import has to do with the transfer of charge across a living membrane, of the mitochondrion for example.

The term "kinetics of electrode processes" is somewhat less encompassing and focusses our attention on the particular steps which are taking place on the electrode itself, without regard to the mass-transfer or phase-separation steps which may have preceded or which will follow those taking place right on the electrode.

Unlike many, perhaps most, chemical processes, the electrochemical ones proceed at rates which are, or can be, controlled by the experimenter using electrical apparatus which is external to the reactor. The experimenter or the production-line worker has available to him a known driving energy, and he can distribute this within the cell and in the external circuitry pretty much in any way he chooses, in order to allow, or to force, the reaction to proceed at the rate he chooses. The OVERALL RATE is expressed as the CURRENT "i" through the cell (Figure 2).

No reactor operates under reversible conditions, since processing is the objective. Many processes are reversible in principle, and electrochemical cells can indeed be made to function more or less ideally and reversibly -- at zero rate of processing, or no current. Under such conditions there may be no losses at all, and the full free-energy of reaction is available, but only over a time-period which is infinite. In the real case of a reactor which is intended to get something accomplished, the rate of processing is finite, and so are the energy losses, both inside and outside the reactor, which accompany the processing.

It is the objective of the applied electrochemical kineticist to identify the lossy steps, wherever they appear, and to make design changes which minimize them. The authors of this paper have been concerned for some years with batteries and fuel cells, and to a lesser extent with electrolyzers and the other electrochemical reactors already mentioned. In these, like all the others, an oxidation process takes place at the anode, and a reduction takes place at the cathode. These two sites of reaction are physically separated from each other in such a way that, in the electron transfer processes, donation of an electron by the one reactant and acceptance of an electron by the other reactant, actually take place at sites which are physically separated from each other by a distance which may be a millimeter to several inches. The rate is expressed as current density, amperes per square centimeter of geometrical area. Since one ampere-second is one coulomb, and since 96500 coulombs is the charge required to oxidize or reduce one equivalent of material, a current density of one ampere per square centimeter expresses a rate of reaction of about 0.00001 equivalents per square centimeter per second, or about 600 atomic layers per square centimeter per second, if only one electron is transferred in the oxidation or reduction of one molecule of reactants.

We decided not to present a developed rate equation but rather to present an overview of the situation, by listing (Figure 2) some of the factors which appear in rate equations in this field. They have familiar counterparts in non-electrochemical processes.

ENERGY LOSS PROCESSES IN AN ELECTROCHEMICAL REACTOR

A Principle. Energy losses at any fixed or chosen rate are manifested as losses of electrochemical potential, that is as losses of voltage: η_A for activation losses and η_{MT} for mass-transfer losses. Thus one can express V , the energy consumed (+) or delivered (-) per unit charge passed, as follows:

$$V = E_{rev} \pm (\eta_A + \eta_{MT})$$

If the overall rate of the process has been fixed at so many amperes, it is inherent that each of the consecutive steps in the charge-transfer circuitry must be proceeding at the same rate -- they are forced to do so, in fact. The slow steps will absorb more of the driving potential than the inherently fast ones. The more reluctant or resistive are the slow steps, the more of the available driving potential will they consume. (The word "consume" was deliberately chosen here to emphasize the fact that the electrochemical potential demanded by the slow process as compensation for it being driven at the chosen rate, ultimately is dissipated as heat--that is, as kinetic energy at the site of the slow process.)

It is clear that the slow steps in consecutive and parallel processes are closely interdependent. Because this is so, it is often quite difficult to identify precisely the step which is the most critical to the design. Hence, it is important to understand both the power and the weaknesses of the diagnostic tools (Figure 3) which the electrochemist has available. Of these the best known amongst electrode kineticists is the Tafel Eqn., which relates the overpotential to the current density. Under conditions in which mass-transfer is relatively rapid compared to the rate of the charge-transfer reaction on the surface of the electrode, the overpotential very often is a linear function of the logarithm of the current density. Under these conditions the slope of the line depends upon the mechanism of the slowest step occurring on the electrode, and its value can be used as a diagnostic tool to identify that slow step. Characteristically it may be a slow electron-transfer reaction between the electrode and some adsorbed species, or it might be a slow combination or disproportionation reaction between two molecular fragments, or it might be a slow desorption of a reaction product, or some other. Sometimes, although not always, the

slopes of these different steps are unique and permit unequivocal assignment of rate-determining steps. This is the simplest, almost the ideal, but a very uncommon case.

More generally, the cell potential becomes split between the two general loss mechanisms, those at or near the electrodes in which the activated complexes are formed, and the others, which may occur anywhere in the total circuit, which have to do in any way with mass transfer.

We can illustrate these points best by reference to an experiment. We could choose the electrolytic production of, or the electrowinning, of Zn, Pb, Ni, or the electrorefining of Cu; or the anodization of Al; or the phosphiding of Ti; or the electromachining of tungsten carbide; or the discharge of the lead-acid battery; or the electrolytic doping of MOS semiconductors; or other solid-state or gaseous electrochemical processes.

A paradigm. For illustration we have chosen the Mg/PbCl₂ seawater cell, which is used in sonobuoys which "listen" for submarines. We have published basic papers on kinetic studies of the reactions of magnesium under these circumstances, have published a design study, and one of the co-authors (JRC) holds basic patents on the formulation of PbCl₂ plates for this purpose. These ideas are incorporated into SSQ batteries currently used by the air force in passive sonobuoys, and further improvements are being sought with respect to high-rate pulse applications in active, "pinging" sonobuoys.

The cell is composed of a sheet of magnesium, a sheet of lead chloride with a current collector (Cu screen) imbedded in it, and an electrolyte of seawater. The main features are given in Figure 4: the reaction, the free energy of reaction, the reversible EMF, the faradaic reactions and the side reaction.

A corrosion reaction occurs between the Mg and the salt solution which not only wastes some of the Mg and produces hydrogen on and in the metal but also polarizes its surface potential down to 1.15V from 1.52, a loss of 0.37 volts (energy per unit charge passed). Here is a reaction whose intrinsic rate is so inhibited by formation of a thin gelatinous film of reaction products that 25% of the energy per unit charge is lost internally before the useful cell reaction has even begun. Where does the energy go? Into hydrogen gas and into heat. Fortunately the specific rate of this side reaction is quite low at room temperature (even lower in cold seawater), so the loss of material is not unacceptable during the life of a 2-hr. or even 8-hr. sonobuoy. But the polarization is significant. One researches the fundamental mechanism and attempts to measure the specific rate constants for the electron-transfer processes and one tries to determine the mechanisms of the inhibition.

The exact mechanism of the inhibition is not known. We tend to view it as an adsorption, on the surface of the magnesium, of the monovalent cations, Mg⁺, some of which slowly desorb to react with water out in the solution and others of which undergo the second charge-transfer reaction to give Mg⁺⁺ which then desorbs into solution. On the same surface, in nearby sites, occurs the corresponding cathodic discharge of hydrogen ion to absorbed H atoms, a necessary step in the hydrogen evolution reaction.

The reaction is an intriguing one. Thus the reaction rate is highly pressure-sensitive due to the role of hydrogen gas, and a mechanism consistent with this intermediate is supported by the observed pressure dependence. Further, the rate is sensitive to the strength of the magnetic field in which it operates. However, we have been unable to observe the Mg^+ via electron-spin-resonance. Others view the reaction as a metallurgical corrosion reaction and explain some of the results, but not the pressure dependence, in terms of mixed-potential theory.

The product of the air oxidation of some magnesium alloys adheres as a tight skin over the metal. This tight skin is protective during storage but must be removed by the seawater before the battery will become fully active. Thus, an initiation period exists for a few seconds in cold seawater. However, a few seconds of inactivity while the sonobuoy is bouncing around after having hit the water and while dropping out its hydrophone is not inconvenient at the practical level.

Some alloys are more easily rolled than pure Mg; normally the AZ61A, a high-purity magnesium alloy which contains 6% Al and 1% Zn, is used. Other alloys, notably those which contain a bit of Li or Sn, show somewhat lower kinetic losses.

The cathode (positive plate) has traditionally been of AgCl. It was recognized in the mid 60's that sooner or later silver would be a critical material on world markets, and we sought alternatives. All the obvious substitute materials, like chlorides of Cu or Sn, had obvious drawbacks. The heavy one, $PbCl_2$, seemed undesirable too, until it was realized that Pb is not really much heavier than silver and that the IR drop through $PbCl_2$ plates would be insignificantly larger than that thru silver at the low current densities in the sonobuoy application. Ways were found to paste with binders, or to cast onto Cu screen, a thin layer of $PbCl_2$. During the reaction with Mg, the $PbCl_2$ undergoes reduction to Pb -- the insulator becomes a conductor.

One could remark that in this case the invention and application preceded the science. Thus, although the kinetics of the anodic oxidation of Pb to $PbCl_2$ have been well worked over, the electrochemical reduction of $PbCl_2$ to Pb has never been investigated properly to our knowledge. The mechanism probably involves the defect-solid-state diffusion of chloride ion through an increasingly porous structure to the solid-solution interface.

But why would one like to know more about the reaction mechanisms? The answer is that, whereas the Mg/ $PbCl_2$ seawater system can be designed to perform well enough (low current, low rate) for "passive" sonobuoys (low power, passive listening receivers), the plates cannot deliver the pulses of power (high rate pulses) needed for "active" sonobuoys (pinging sonic transmitter plus passive listening receiver). Not really knowing what the energy-loss processes or slow steps are, one does not know how to design around them. We need to know what factors influence the rate, and by what mechanism, and we would like to know what is the quantitative relationship between overall rate and each of the major factors, under the pulse-power (high-rate) conditions.

A Perspective. One could have chosen to illustrate these fundamental loss mechanisms by drawing an example from many other applied

electrochemical processes of importance to Canada (Figure 5). The economic giants are metal-winning and refining, the chlor-alkali and electroplating industries, and to a lesser extent hydrogen production. The underlying principles are the same.

In the electrowinning of Zn and Pb the immensity of the electrodes and the sheer size of the cell rooms are impressive. Thus at the Ray-O-Vac plant, where flashlight cells are made at a rate of a million per day, the slow step is to move them out the front door. The same comment is true about handling Zn and Pb at COMINCO in Trail, Cu at the Canadian Copper Refineries in Montreal, Al from ALCAN at Arvida, and Ni from INCO at Port Hope.

In the electroplating industry not only is the practitioner often poorly informed about the composition of the solutions he buys, but a slight compositional change is so influential on brightness of deposit that he has to replace and waste valuable chemicals. Some recovery can be achieved, of course.

Product removal is critical to continuity of processing in some cases. Although the turnover rate of electrocatalysts can be extremely high, as high as for an enzyme, it can be disastrously inhibited by reaction products or other species which remain adsorbed on the surface. Commercial production of organics is impeded by this problem.

The annual loss of metals alone by corrosion, estimated to be \$0.6B in Canada, is staggering enough, but the secondary effects in down time, structural-repair and -replacement costs may be 5-10 times the replacement costs of the metal alone.

Hence, there are good practical reasons for wanting to have a better understanding of the fundamental electrochemical kinetics of many, many electrode processes. For a country in which electrochemical industry still contributes a sizeable 2% to the whole GNP, we are simply not endowed with enough good applied electrochemical kineticists who are practicing effectively.

It is indeed sad that terminology has impeded the easy communication between general kineticists and electrochemical kineticists. The basic ideas are pretty much the same.

OTHER ITEMS OF CURRENT INTEREST

The authors remain interested in sulfur compounds. Some current interests are listed in Figure 6. Some sulfur compounds are promoters; some are poisons.

First of all, the Pb-acid battery accepts charge only at a low rate at low temperatures. Even the rate-determining steps at low temperatures (0 to -40°C) still are not known for sure. The rate of conversion of lead sulfate to lead dioxide, at the positive, limits the overall rate. Persulfates and peroxides are formed at low temperatures, and these probably inhibit the oxidation recharge processes. Low temperature electrolysis followed by L-R spectral studies of the anolyte are in progress. It may be useful that WAA has learned recently that low temperatures favor the formation of sulfate over bisulfate, just as does increased pressure at 25°C .

Several years ago two of the authors (EJC and JRC) did a kinetic study of the gamma-radiation-induced deactivation of chymotrypsin and its protection by -S-S- containing amino acids. Then JRC studied and published on the electroreduction of sulfur in DMSO solutions, and tried to unravel the phenomenon of the opening up of the molecular ring of sulfur during the electroreduction process. Spin-resonance and spectroscopic techniques helped describe the phenomenon, but the kinetics still remains obscure.

Colleagues at DREO have become interested in the layered disulfides of Ti and Mo. (These are candidate positive-plate materials in highly energetic batteries based on the reaction of lithium metal with them in molten salt and in organic electrolytes. Explosive side reactions have to be understood and controlled in the case of organic electrolytes.) Further, the use of waste SO_2 as depolarizer in metal-electrowinning cells looks very attractive from the point of view of electricity savings.

Sulfur compounds are highly poisonous in the operation of hydrogen-oxygen fuel cells. All the sulfur has to be taken out of the hydrogen which is fed to the electrocatalyst of the fuel cell, otherwise the power (proportional to the rate of oxidation of hydrogen on the surface) decreases with time because of inhibition by refractory sulfur-containing polymers adsorbed on to the active sites.

Photoelectrochemical events received an important stimulus in 1973 with the discovery that electrolysis could be accomplished at lower cell potential if GaAs semiconductors were used as anodes and photolysed during the process. Many researchers have already been attracted by this discovery, including some well established fundamental-electrochemical kineticists. Practical progress so far has not been spectacular, although several practically minded groups, including ourselves, have made attempts to develop photoelectrochemical devices. One basic problem is the chemical instability of the semiconductor surface under simultaneous photolysis and anodic oxidation. In kinetic terms, we theorize that the same activated complex formed on the surface with the absorption of the photon can proceed either to the discharge of hydrogen or to a bond-breaking step in the semiconductor.

Finally, we note that specific ion electrodes, made of organic semiconductors whose interface with aqueous solutions responds to specific organic redox systems in the solution, are becoming very important in practice. The studies emanating from this development are opening up new opportunities in bioelectrochemistry, or biophysical chemistry. The application of these techniques not only for the understanding of the fundamentals of redox reactions, but also for control of the concentrations

of essential enzymes and mediators and anti-cancer drugs in biological tissue is already in progress in other laboratories. This work may become the legacy of applied electrochemical kineticists of the 1980's.

PROSPECTS FOR ROOM TEMPERATURE MOLTEN SALT CELLS

Electrochemical kinetics is concerned with aqueous, non-aqueous, gaseous, molten salt and solid-state electrolytes. One of the newest intriguing electrolytes is a molten salt which is liquid at room temperature. Over the past few years we have watched the emergence of electrorefining of Ti at 800°C; have done research on metaphosphate electrolytes at 650°C; have contributed to the development of the rechargeable Li/FeS battery, which operates in a moisture-free molten salt of eutectic chlorides at about 400°C; have experimented with the chloroaluminates at 200°C, but shied away from the thiocyanates, mixtures of which melt about 100°C, because of their instability as working electrolytes.

Last year King and Osteryoung independently published on a series of mixed salts made from alkylpyridinium chlorides on the one hand and aluminum chloride on the other. Figure 7 shows the main features. We made N-n-butyl pyridinium chloride, condensed it with $AlCl_3$ to give a series of liquids at RT. Osteryoung's L-R spectra showed the presence of the tetrachloroaluminate and the substituted pyridinium cation as well. Our own scanning-voltammetry confirms King's and Osteryoung's work that the "melts" are indeed stable over a useable voltage range and may be suitable battery electrolyte.

The voltammogram of aluminum in Figure 8 indicates reversibility and stability of a redox couple based on Al metal. It can be used as a reference electrode in these melts, and possibly as a rechargeable negative plate.

Chronopotentiometry of titanium (Figure 9) shows that it can in fact be oxidized and reduced electrochemically in this salt, although with interference from aluminum. Finally, we find that although Li seems to be rechargeable (Figure 10), the interference from Al, its attack of the substituted pyridinium ion and its tendency to wander out into the electrolyte, militate against the practical use of Li in a rechargeable battery, at least in the acidic electrolytes containing excess $AlCl_3$ which have been studied so far.

In this work a dry-box, careful attention to purity, and sensitive electronic apparatus are essential. The ultimate usefulness of room-temperature molten salts may be determined more by cost factors than by chemical stability or conductivity. In many cases the traditional electrochemical-cell systems still hold inherent advantages of simplicity and manufacturability. But the newer systems sometimes provide the ONLY way to accomplish some processes involving light, strong oxidants and reductants.

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General:

Advances in Electrochemical Engineering; J. Electrochem. Soc.; Elektrochimya; Electrochimica Acta; Corrosion; J. Appl. Electrochem.; Denki Kagaku; Modern Electrochemistry (series); J. Power Sources.

EPILOGUE

This particular session of the Symposium on Chemical Kinetics, which is dedicated to Prof. K.J. Laidler, highlights papers on ELECTROCHEMICAL KINETICS. The Chairman, Prof. B.E. Conway, Prof. Laidler's colleague at Ottawa University, is world-renowned in this field. The co-authors of this invited lead paper all were former pupils. The other speakers in the Session, Drs. C.L. Gardner, Defence Research Establishment Ottawa, B.F. MacDougall, National Research Council, and F.R. Smith, Memorial University, his colleagues in spirit, have international reputations for their own research work in this field.

Perhaps the leading electrochemical kineticist amongst Laidler's former pupils is Dr. J.P. Hoare, whose publications and books on electro-machining, the oxygen electrode and chromium deposition are highly respected. He could not come. Another former pupil, Sr. Claire Markham, who is a specialist on surface electrochemical problems, was able to be present, as were several others "who do" electrochemistry part-time in the course of their duties in general physical chemistry -- some in teaching, others in industry or in government. Because of the intrinsic as well as practical importance of electrochemistry (some call it "The Queen Bee of the Sciences"), it is perhaps not surprising that several of Prof. Laidler's students have turned that way.

SOME TOPICS IN APPLIED ELECTROCHEMISTRY

1. ON ELECTROCHEMICAL & ELECTRODE KINETICS
 - cross-talk
 - energy loss processes
2. SOME APPLIED KINETICS PROBLEMS
 - in the Mg/PbCl_2 battery (demonstration)
 - in electrochemical reactors in general (discussion)
3. PRACTICAL ELECTROCHEMICAL PROBLEMS WITH SULFUR COMPOUNDS
 - a litany
4. OF WHAT USE IS A 25°C MOLTEN SALT?

FACTORS IN EXPRESSIONS OF ELECTROCHEMICAL RATE " i "

RATE " i " = f (ACTIVATION & MASS-TRANSFER FACTORS)
 quantitatively descriptive, not predictive

● FOR ACTIVATION PROCESSES

FREE ENERGY OF ACTIVATION
 ELECTROCHEMICAL POTENTIAL
 ELECTRODE POTENTIAL
 ADSORPTION PARAMETERS (θ , ΔG_{ads})
 SPECIFIC RATE CONST/EXCHANGE CURRENT
 THERMAL FACTORS
 TRANSMISSION OR TUNNELING OR EXCITATION FACTORS

● FOR MASS TRANSFER PROCESSES

ION MOBILITY IN ELECTROLYTE
 MOBILITIES IN SEPARATORS OR SURFACE FILMS
 ELECTRONIC MOBILITY & DIMENSIONS OF ELECTRON CONDUCTORS
 DIFFUSION COEFFICIENTS
 PRESSURE GRADIENTS IN CONVECTIVE FLOW
 FLUIDITY IN FORCED FLOW
 SOLID-STATE TRANSFER IN ACTIVE MASSES
 GEOMETRICAL DIMENSIONS
 THERMAL GRADIENTS

$$i \text{ } 1A/cm^2 \approx 10^{-5} \text{ EQUIV}/cm^2 \text{ SEC} \approx 600 \text{ ATOMIC LAYERS}/cm^2 \text{ SEC}$$

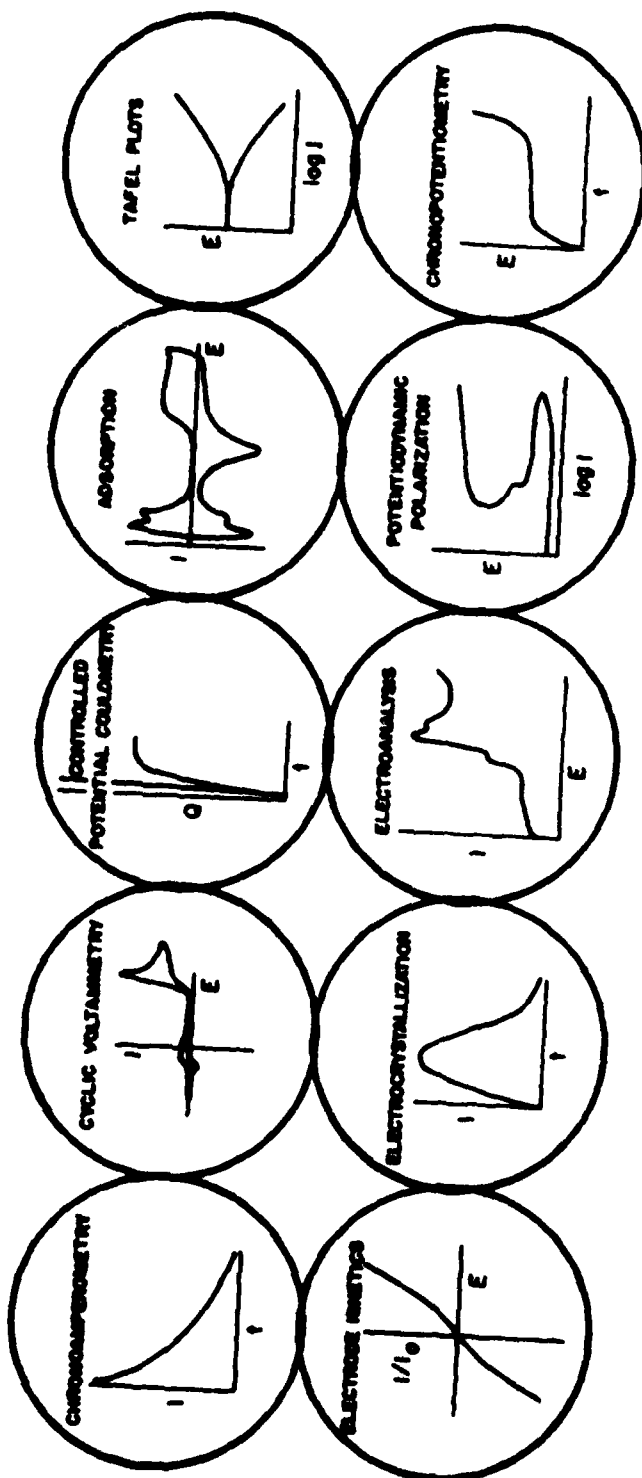
WITH WHAT DIAGNOSTIC EXPERIMENTAL RELATIONSHIPS SHOULD WE HAVE LAB EXPERIENCE?

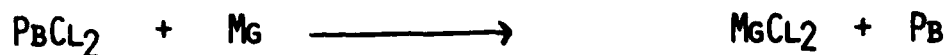
● $i^P \cdot C = \text{const}$	PEUKERT capacity formula
● $\eta \propto i$	KOHLRAUSCH ohmic law
● $\eta \propto \log (i - i_L)$	GLASSTONE diffusion law
● $i \propto 1/\sqrt{t+t_0}$	DELAHAY rundown eqn.
● $\eta \propto \log I$	TAFEL activation law
● $\eta \propto \log (t+t_0)$	ARMSTRONG & BUTLER potential-decay expression
● $\rho(dv/dt) = q\text{grad}P + \nu \nabla^2 v + F$	NAVIER-STOKES equivalence in hydrodynamic flow

- PLUS -

The Laws and Equivalences Bearing the Names of

ARRHENIUS	FICK	OHM
DE GROOT	HENDERSON	ONSAGER
DONNAN	LAPLACE	USSING
FARADAY	NERNST	And Others



Mg/PbCl₂ SEAWATER BATTERYOVERALL REACTION

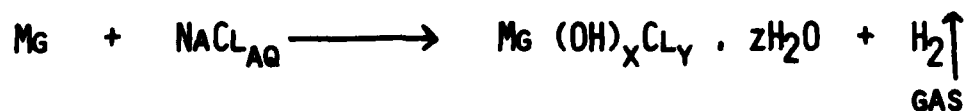
$$\Delta G^\circ = -1.87 \text{ kJ MOLE}^{-1}$$

$$(-78 \text{ KCAL/MOLE})$$

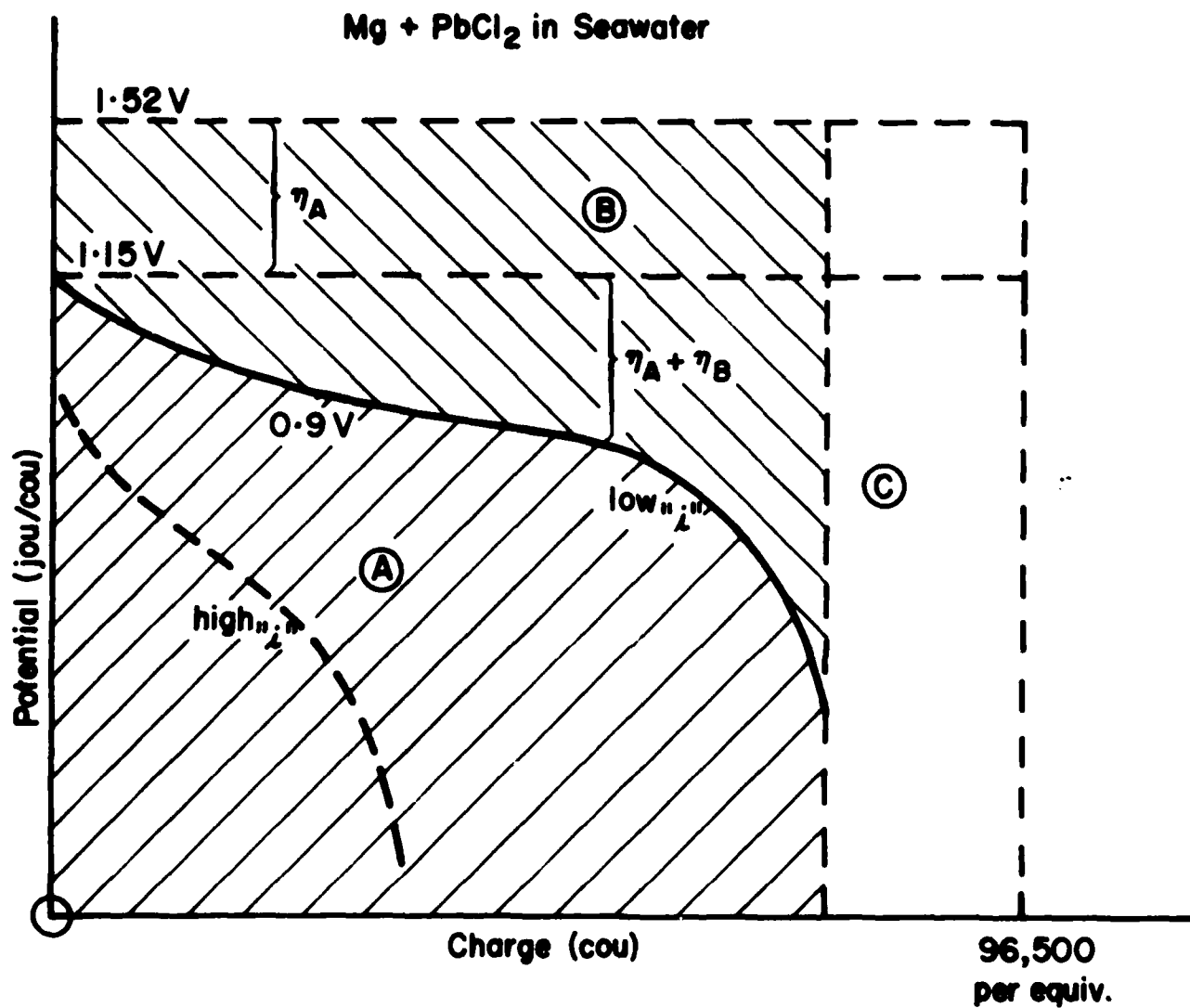
$$E_{\text{REV}}^\circ = 1.52\text{V}$$

$$\text{THEORETICAL ENERGY DENSITY} = 971 \text{ kJ kg}^{-1}$$

$$(123 \text{ WH/LB})$$

FARADAIC REACTIONSMAIN SIDE REACTIONOPERATING CELL VOLTAGE

$$\sim 0.8 \text{ TO } 1.0 \text{ V} \quad (\text{LOWER AT HIGH RATE})$$



- Energy Diagram : (A) Electrical Energy Output
 (B) Energy Loss as Heat and Chemicals
 (C) Covered Mg or PbCl₂

OPPORTUNITIES IN APPLIED (ELECTRO)CHEMICAL KINETICS

PRODUCTION**

1. METAL PRODUCTION
2. CHLOR-ALKALI PRODUCTION
3. PLATING AND ANODIZING
4. BATTERIES
5. ELECTROLYSIS (H_2 & O_2)
6. ORGANICS
7. ELECTROMACHINING

CONSERVATION

1. CORROSION PREVENTION*
2. ENERGY-STORAGE SYSTEMS
3. ELECTROANALYSIS
4. BIOELECTRIC CONTROL

** ANNUAL CONTRIBUTION TO GNP
\$2 BILLIONS

* ANNUAL LOSS
\$0.6 BILLION

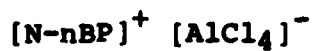
KINETIC STUDIES WITH SULFUR COMPOUNDS AT DREO

- H_2SO_4
- K_{EQ} AS FN (T, c, P)
 - ANODIC FORMATION OF +7 AND +8 SULFUR AT $-30^\circ C$ IN LEAD-BATTERY ACID
- ELEMENTAL S
- CATHODIC REDUCTION:
IN MOLTEN CHLOROALUMINATES
IN DMSO + SALTS
- TiS_2 , MoS_2
- ELECTROREDUCTION AND OXIDATION AS LI INTER-CALATION CPDS FOR RECHARGEABLE LI CELLS
- SO_2 & $SOCl_2$
- CATHODIC FORMATION OF CHARGE-TRANSFER COMPLEXES IN NON-AQUEOUS MEDIA IN LI CELLS
 - ANODIC DEPolarizer IN METAL ELECTROWINNING CELLS
- "CPDS-S"
- (UNIDENTIFIED) INHIBITORS OF ELECTROCATALYSTS IN FUEL CELLS
- Na_2S
- INHIBITION OF RECOMBINATION OF SURFACE CHARGES PRODUCED BY PHOTONS ON CdSe IN PHOTOELECTRO-CHEMICAL ENERGY-CONVERSION CELLS
- TECHNIQUES :
- ELECTROCHEMICAL
SPECTROSCOPIC
ANALYTICAL

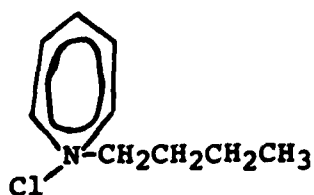
A DRY, ROOM-TEMPERATURE MOLTEN SALT ELECTROLYTE



strongly
exothermic



liquid at RT



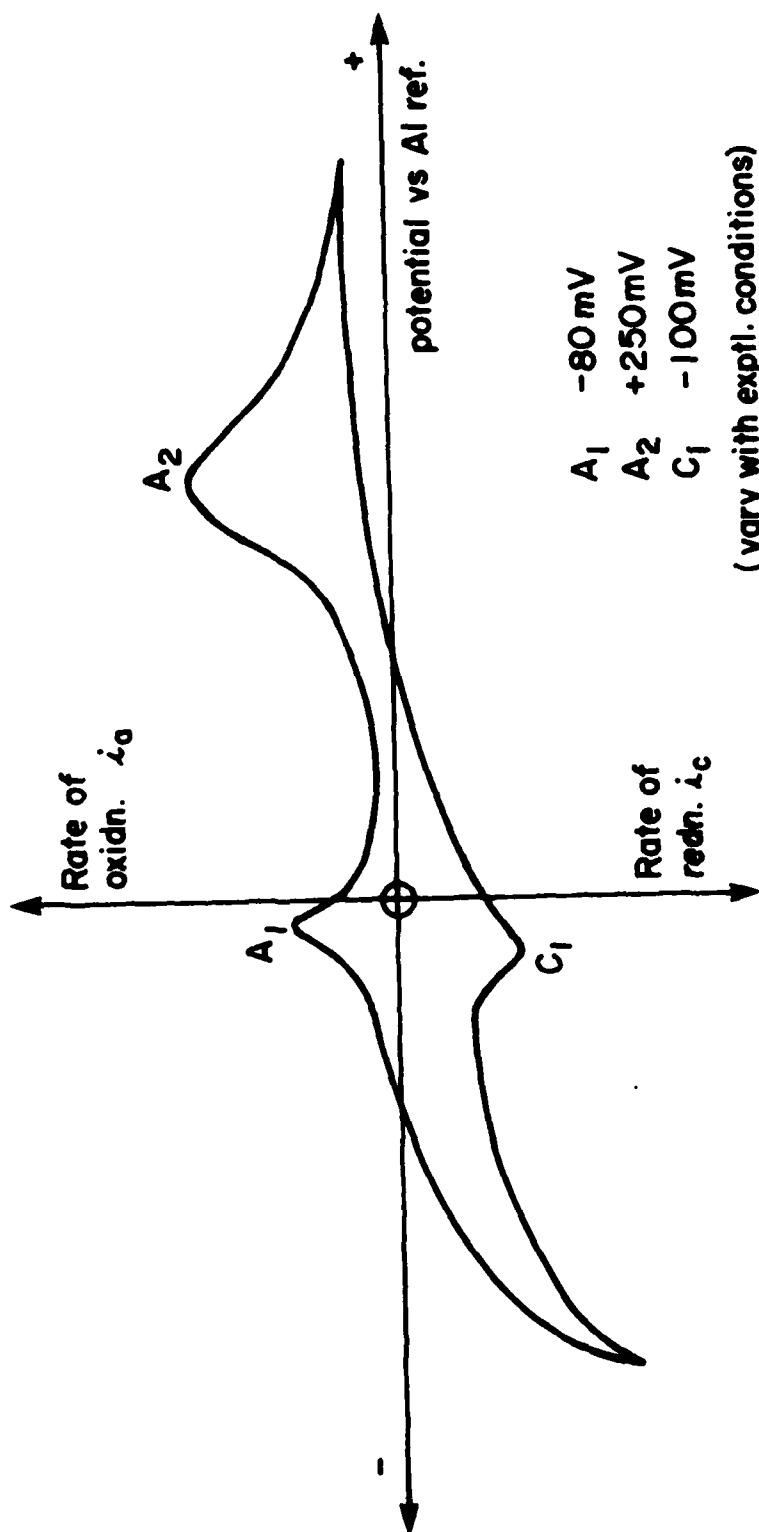
N - normal Butyl Pyridinium Chloride

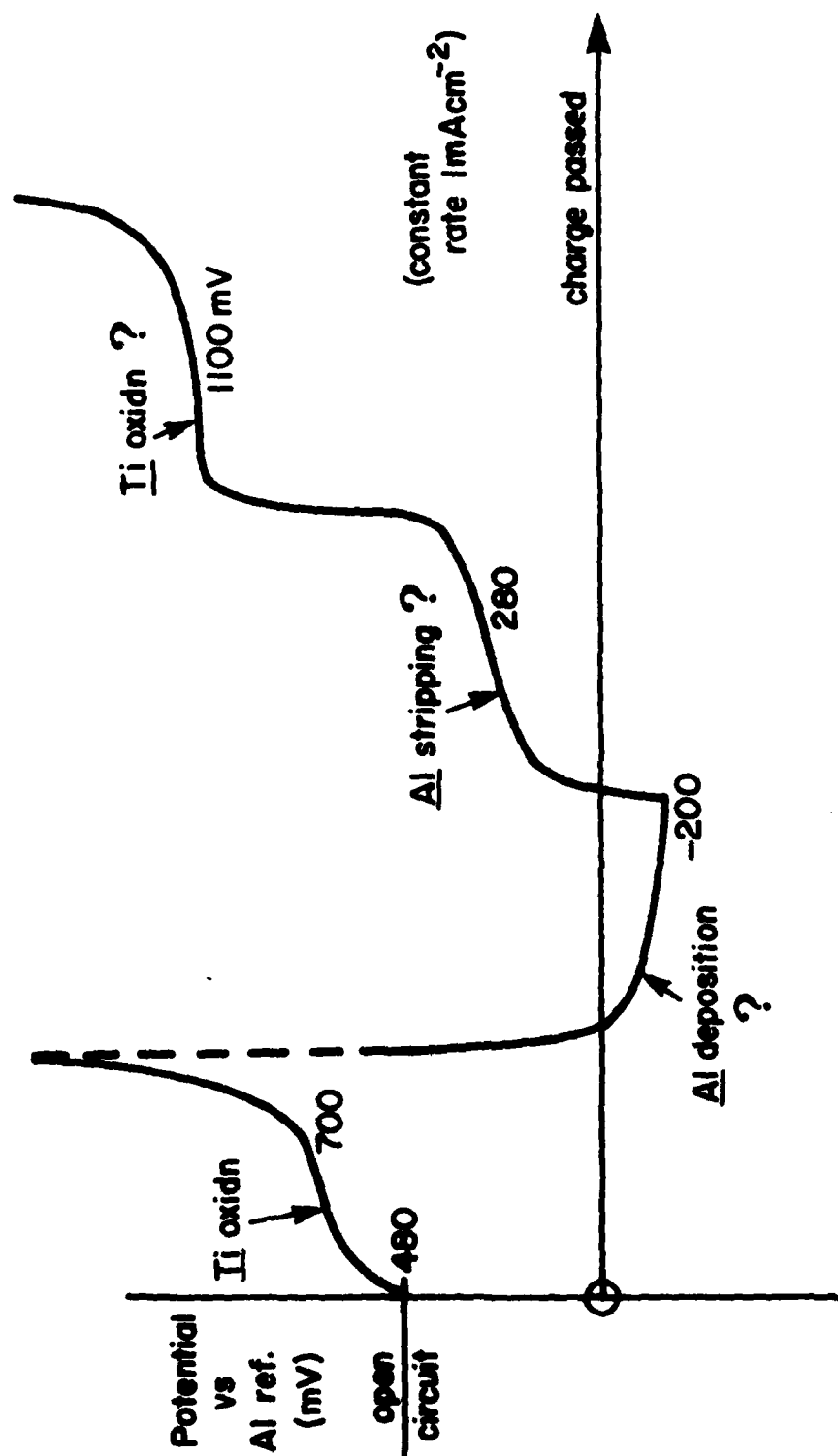
ROOM TEMP. MOLTEN SALT STUDIES

10

APPENDIX 1

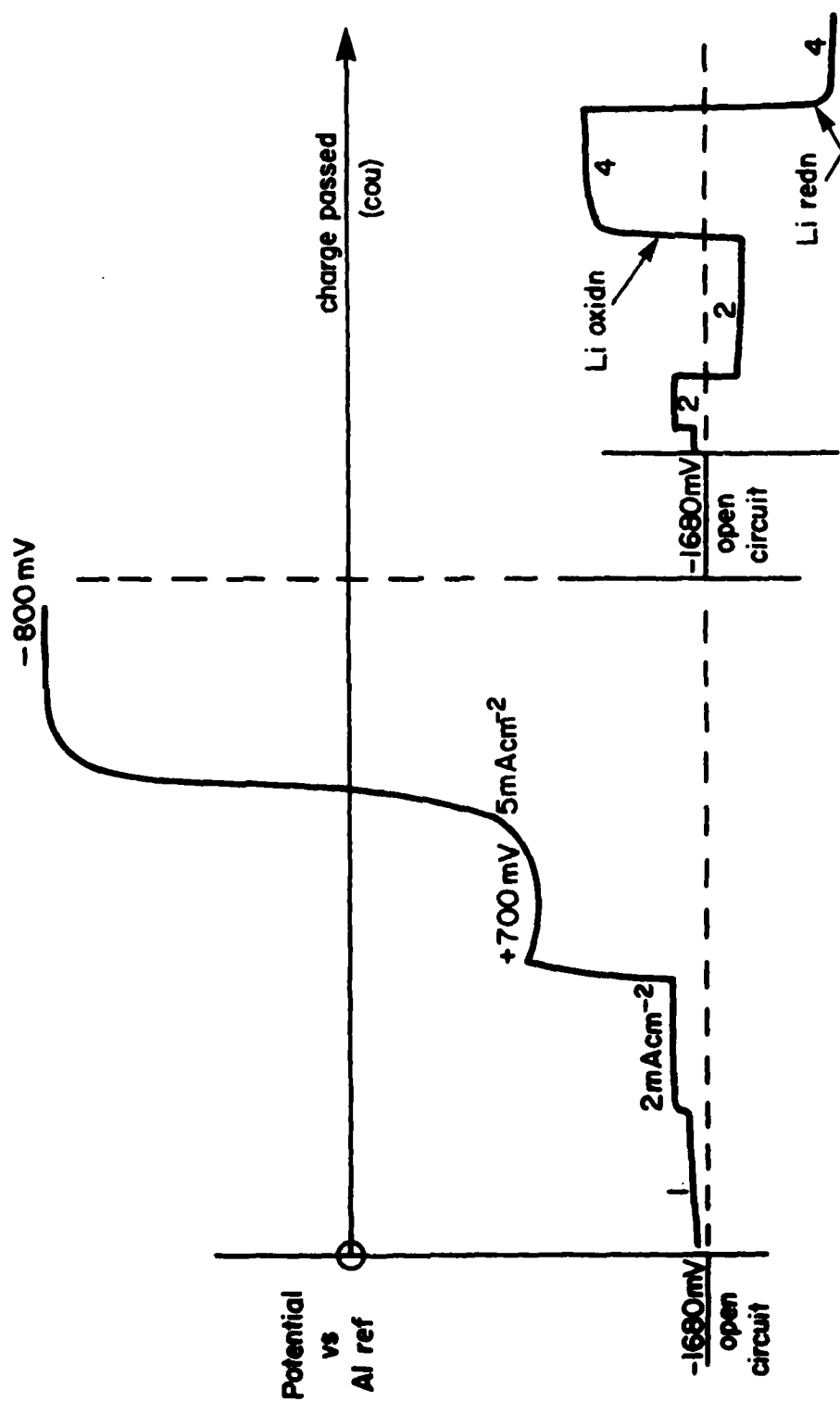
Oxidn. - Redn. Activity of Al in nBP-TCA at 25°C





Electrodeposition of Al on Ti at 25°C in nBP-TCA ?

Oxidn. and Redn. of Li Metal at 25°C in nBP-TCA at Constant Rates "i"



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13. ABSTRACT (Unclassified) <p>The designer of an electrochemical reactor attempts to minimize the inevitable energy losses associated with irreversible processes. The slow steps, which are the greatest offenders, have to be identified. Fortunately, diagnostic techniques have arisen from developments in electrochemical kinetics -- not only for electrode processes but also for the mass-transfer and phase-separation processes which occur in series and parallel in every electrochemical reactor.</p> <p>Although electroplating, anodizing and electromachining, electrowinning and electrosynthesis are acknowledged as activities also of great importance to Canadian life, in this paper the examples will be drawn from the authors' work on batteries and fuel cells, i.e. from attempts to identify the slow steps and the wasteful side reactions, and to design around them.</p> <p>The mutual influence of theoretical ideas and practical achievements is the unifying theme of this lecture. ←</p>		

KEY WORDS

kinetics
 electrochemical kinetics
 electrolyte
 seawater battery
 molten salt

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